Suppression of f-Electron Itinerancy in $CeRu_2Si_2$ by a Strong Magnetic Field

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The valence state of Ce in a canonical heavy fermion compound $CeRu_2Si_2$ has been investigated by synchrotron X-ray absorption spectroscopy at 1.8 K in high magnetic fields of up to 40 T. The valence was slightly larger than for the pure trivalent state (Ce^{3+}: f^1), as expected in heavy fermion compounds, and it decreased toward the trivalent state as the magnetic field was increased. The field-induced valence reduction indicates that the itinerant character of the $4f$ electrons in $CeRu_2Si_2$ was suppressed by a strong magnetic field. The suppression was gradual and showed characteristic magnetic field dependence, which reflects the metamagnetism around $H_m \sim 8$ T. The itinerant character persisted, even at 40 T ($\sim 5H_m$), suggesting that the Kondo bound state is continuously broken by magnetic fields and that it may completely collapse at fields exceeding 200 T.

The correlation between localized and itinerant electrons is one of the most intriguing subjects in condensed matter physics. Heavy electrons emerge in rare-earth and actinide compounds and give rise to exotic phenomena such as non-Fermi liquid behavior [1–3] and unconventional superconductivity [3–5] because of their strong correlation. The magnetic quantum critical point (QCP) in the Doniac model [2, 6] is one of the most important concepts for understanding the low-temperature physics of heavy fermion (HF) systems. However, another type of QCP, which is caused by the valence transition (VTQCP),[7, 8] has been proposed as the origin of the unusual superconductivity, such as that observed in $CeCu_2Si_2$ [9] and also as the origin of the metamagnetism inYb-based HF systems [8, 10].

Most of the HF systems contain Ce or Yb. The occupation number of the $4f$ electron in the orbital (n_f) is close to 1 for Ce, and in Yb, the occupation number of the $4f$ hole (n_h) is ~ 1. The $4f$ electrons acquire an itinerant character because of the strong hybridization with the conduction electrons. The energy level of the correlated $4f$ electrons is near the Fermi energy, because the significant electron-electron many-body interaction causes the electrons to become itinerant HFs. The degree of the itinerancy is determined by the strength of the electron interaction. The itinerant character manifests itself in the deviation of the occupation number of the f electron or hole from unity: $1 - n_f$ or $1 - n_h$. According to the Gützwiller approximation, the deviation $1 - n_f$ can be expressed by $1 - n_f = \frac{kT_F^*}{\Gamma}$, where kT_F^* and Γ correspond to the kinetic energy of the f electrons with the electron interaction and that without the interaction, respectively.[11] In HF systems, $1 - n_f$ must be very small but finite, indicating that the electrons are highly localized and only slightly itinerant.

The direct observation of the valence of Ce and Yb in heavy fermion compounds in high magnetic fields is particularly desirable because the magnetic field dependence of n_f and the change in the itinerant behavior of the electrons can be directly measured. However, it is not easy to determine the precise magnetic field variation of $1-n_f$ or $1-n_h$ experimentally, because they generally have values smaller than 0.1 in HF systems; the field dependence is expected to be of the order of 0.01 or smaller. Therefore, the change in the behavior of the heavy electrons caused by a magnetic field has rarely been studied in terms of the valence state.

$CeRu_2Si_2$ is a canonical HF system and has been attracting considerable attention for its metamagnetism around $H_m \sim 8$ T.[12] It was proposed that the transformation of the $4f$ electrons from the itinerant to the localized state induced by a magnetic field (so-called the Kondo breakdown) could be observed based on the change from a large to small Fermi surface. [13] However, it was later found that the change in the Fermi surface is not necessarily concrete evidence of the transformation of the f electrons [14–16]; the possible change in the behavior of the f electrons is still controversial. [17]

We have performed synchrotron X-ray absorption spectroscopy for $CeRu_2Si_2$ in high magnetic fields of up to 40 T at 1.8 K. The magnetic field caused significant changes in the X-ray absorption spectrum near the Ce-L_3 edge, suggesting a change in the Ce valence toward the pure trivalent state. The suppression of the f-electron itinerancy and the magnetic field dependence are discussed.

The X-ray absorption experiment was carried out at beamline BL22XU of SPring-8. Pulsed high magnetic fields of up to 40 T were generated by a miniature pulsed magnet.[18] The duration of the magnetic field was 1 ms and the repetition rate was 4 pulses per hour for a 40 T measurement. The magnet and sample were cooled to 1.8 K by using an ILL-type He gas flow cryostat. The X-ray absorption spectrum was taken by a direct transmission method. The details of the experimental techniques have previously been described. [18] A single crystal of $CeRu_2Si_2$ was grown by the Czochralski pulling method. The crystals were powdered and mixed with

epoxy resin so that the effective thickness was appropriate for an X-ray absorption intensity of $\mu t \sim 1$, where μ and t are the absorption coefficient and the thickness of the sample, respectively. The c-axes of the powder crystals were aligned by means of a steady magnetic field of 14 T when the epoxy resin was solidified. The diameter of the powder was μm. Diluting fine powders in epoxy resin avoided Joule heating of the sample by a pulsed magnetic field. The high magnetic field magnetization data was obtained by the induction method using a conventional pulsed magnet.

The X-ray absorption spectra (XAS) at 1.8 K in a zero magnetic field and at 25 T are shown in Fig. 1. The magnetic field was applied in parallel to the c-axis of the sample. Although there is a clear magnetic field effect, which is discussed later, the spectrum at 25 T was very similar to that at 0 T. The absorption peak near 5.727 keV was the white line at the Ce L_3 absorption edge in the trivalent state (Ce^{3+}: f^1). A small absorption band was observed in the spectrum around 5.735 keV, which can be attributed to the tetravalent state (Ce^{4+}: f^0) [19]. The spectrum shape fitting was performed using the standard Lorentz and arctangent functions with a linear background. The solid curve, dotted, and dot-dashed curves are the results of the spectrum fitting to the zero magnetic field curve. The dot-dashed and dotted curves represent the f^1 and f^0 states, respectively, and the solid curve represents the whole shape of the spectrum. The valence v was directly determined by the relative intensity of the absorption bands, $v = 3+I(f^0)/(I(f^0)+I(f^1))$, where $I(f^0)$ denotes the absorption intensity of the f^0 absorption band and $I(f^1)$ denotes that of the f^1 absorption band. The observed f^0 and f^1 contributions are 0.053 and 0.947, respectively, and the Ce valence was calculated as $v = 3.053 \pm 0.02$ ($1 - n_f = 0.053 \pm 0.02$) at zero magnetic fields.

The f^0 component of $CeRu_2Si_2$ at 20 K was reported to be 0.06 by the photoemission spectroscopy and the soft-X-ray absorption spectra with the analysis using the impurity Anderson model. [20, 21] Hence, the estimation of the f^0 component in our XAS study at 1.8 K seems to be in good agreement with the previous reported value. Since we did not take f^2 contribution into account in this work, we may overestimate n_f. Actually n_f was deduced to be 0.013 at 20 K if we assume that there is the f^2 contribution of 0.05. [20, 21] However,in terms of the Kondo breakdown scenario, the $f^0 \rightarrow f^1$ transformation is the dominant magnetic field effect. Moreover, we can safely assume that the f^2 state is much less sensitive to magnetic field than the $f^1 \leftrightarrow f^0$ transformation similarly to the pressure variation of Ce valence in $CeCu_2Si_2$. [9] Therefore, since $1 - n_f$ obtained in this work corresponds to the f^0 component and should directly reflects the degree of the itinerancy, a small correction by the f^2 component is not important for evaluation of the magnetic field effect on the valence state in the present study.

The change in the spectrum induced by the magnetic field was very small; therefore the spectrum at zero magnetic field was subtracted from the spectrum at finite magnetic fields in order to see the field evolution of the spectrum clearly. The difference XAS (dXAS) at different magnetic fields are shown in Fig. 2. The open circles are the experimental results and the solid curves are derived from the fitting curves. The positive and negative peak structures appeared around 5.725 and 5.735 keV, respectively; these energy positions correspond to the absorption bands from the f^1 and f^0 states shown in Fig. 1. This characteristic feature evolved as the magnetic fields increased, suggesting the f^1 state became more prominent, whereas the f^0 state diminished. The intensities of the f^1 and f^0 band were used as the fitting parameters and the fitting results accurately reproduced the characteristic features of the dXAS (Fig. 2). Therefore, the valence decreases toward the trivalent state as the magnetic field increases. When the same experiment was performed with the magnetic field perpendicular to the c-axis ($H \perp c$), the dXAS was almost flat with no significant features even at 25 T, suggesting that there was no field dependence of the valence state when $H \perp c$. Since the magnetization for $H \perp c$ is more than 10 times smaller than that for $H \parallel c$, it is expected that the magnetic energy gain for $H \perp c$ is not sufficient to induce a suppression of the f-electron itinerancy. The Ce valence was evaluated at different magnetic fields through the fitting analysis, and decreased as the magnetic field increased. The valences are shown in parentheses in Fig. 2. The experimental error in the relative change of the valence from the zero field value was about ± 0.003, which is too large to allow for detailed discussion of the magnetic field dependence of the valence.

To observe the magnetic field variation of the valence more precisely, we focused on two particular energy positions, 5.725 and 5.737 keV. The measurements for the

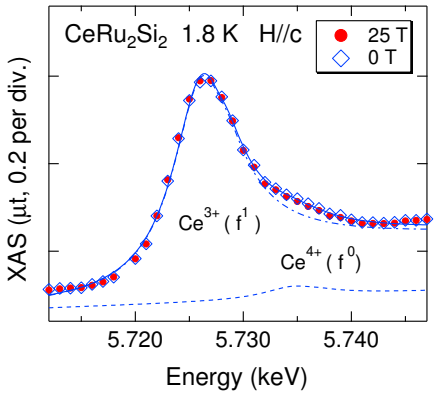

FIG. 1. X-ray absorption spectra near the Ce L_3 edge at 0 and 25 T. The solid, dotted, and dot-dashed curves are the results of the spectrum fitting to the zero magnetic field spectrum.

magnetic field dependence of the absorption intensity were repeated 10 times for each energy and the average was taken (Fig. 3). The change in the absorption intensities at the two energy positions should follow the change in the components of the f^1 and f^0 states. It is found that the change in the absorption intensity at low magnetic fields was small and the change rate increased under magnetic fields around 8 T.

Assuming that only the intensity changed and that the shape and the energy shift of the f^1 and f^0 absorption bands were not altered, the magnetic field dependence of the valence was determined from the results shown in Fig. 3. In Fig. 4 (a), the valence is plotted as a function of magnetic field, and the magnetization (M) and its magnetic field derivative (dM/dH) at 4.2 K are shown as a function of the magnetic field in Fig. 4 (b) for comparison. In the M and dM/dH curves, the metamagnetic transition is clearly visible at 8 T (H_m). The valences were in good agreement with those obtained by XAS shown in Fig. 2 within the experimental error. Because of the better signal to noise ratio of the results shown in Fig. 4, the unusual magnetic field dependence of the valence was visible. The valence decreased slightly in low magnetic fields and the rate of the decrease was larger when the magnetic field was higher than about 8 T; this magnetic field was defined as H_v. The two dashed lines labeled (1) and (2) show the slope of the valence change in low and high magnetic fields around H_v. It was clear that H_v corresponded to the metamagnetic transition field, H_m. Because H_m shows almost no temperature dependence, [12] the temperature difference between 1.8 and 4.2 K is not important as we compare H_v and H_m. The valence gradually decreased and continued to change even at magnetic fields higher than H_m. The valence decreased even at 40 T, although the metamagnetic transition was probably complete above 20 T.

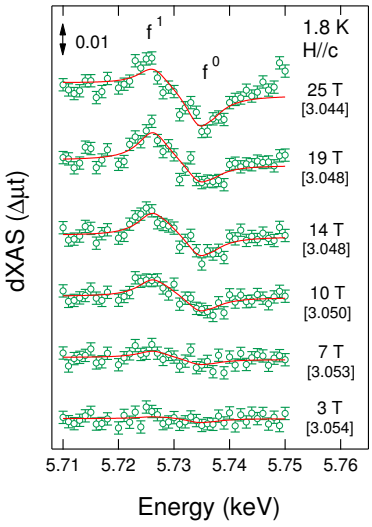

FIG. 2. Difference spectra obtained by subtracting the XAS at zero magnetic fields from that at finite magnetic fields. The open circles are the experimental results and the solid curves were obtained from the XAS fitting. The values in the parentheses are the valences deduced from the fitting analysis. The relative error from the zero field valence ($v = 3.053$) was about ± 0.003.

The significance of the decrease in the Ce valence when the magnetic field was applied parallel to the c-axis of the crystal was examined. It is generally accepted that the HF state is broken if a strong enough magnetic field is applied. This is because the heavy fermion state is reached through the Kondo singlet bound state, and the singlet state can be broken if the Zeeman energy exceeds $k_B T_K$, where the k_B is the Boltzmann constant and T_K is the Kondo temperature. For $CeRu_2Si_2$, shown in Fig. 4, the corresponding Zeeman energy is about 14 K which is comparable to the $T_K \sim 24$ K, [12] because the magnetization is roughly 1 μ_B at 10 T. Hence, we propose that the Kondo bound state begins breaking at the metamagnetic transition. This qualitative explanation is the same as that given for the Fermi surface shrinkage at the metamagnetic transition. [13] However, if the f electron becomes completely localized because the Kondo singlet state is broken, the Ce valence state should become purely trivalent and independent of magnetic fields. According to our x-ray absorption results, the f^0 component was still finite value and continued to decrease with the magnetic field, even at 40 T. Therefore, it is found that the itinerancy of the electrons is gradually suppressed by the magnetic field and the suppression becomes prominent at the metamagnetic transition field H_m. The suppression rate becomes small again around 19 T where the lines (2) and (3) cross, and the metamagnetic transition also appears to finish according to the dM/dH curve. The suppression continues even at magnetic fields as strong as $5H_m$.

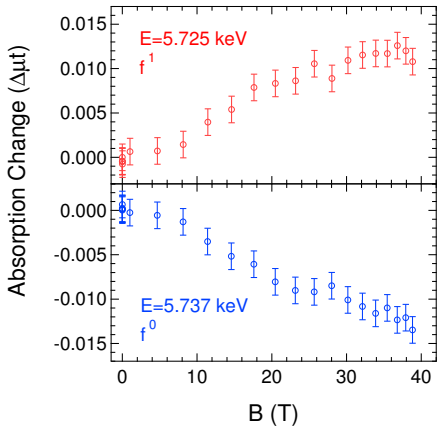

FIG. 3. Change in the absorption intensity at 5.725 and 5.737 keV induced by magnetic fields.

The valence fluctuation phenomena around H_m in $CeRu_2Si_2$ may be related to the QCP of the valence transition (VTQCP), as has been suggested in other heavy fermion compounds.[10, 22] The Ce valence of $CeRu_2Si_2$ was thought to be nearly trivalent and stable in magnetic fields. However, we have discovered that the valence depends on the applied magnetic field and changes by about 0.005 around the metamagnetic transition (8-18 T). The valence change was several times smaller than that of $YbAgCu_4$ [25] a heavy fermion material that exhibits metamagnetism, which is probably caused by the VTQCP. It is not clear at the present how far away $CeRu_2Si_2$ is located from the VTQCP; [10, 22] and the mechanism of the metamagnetic transition in $CeRu_2Si_2$ should be re-examined.

Another interesting finding is that the valence change can quantitatively explain the large magnetovolume effect in $CeRu_2Si_2$ [23]. When 5.221 and 4.661 Å were used for the ionic radii (r) of Ce^{3+} and Ce^{4+}, respectively, [24] the relative change in the radius $\frac{\Delta r}{r}$ was 6.47×10^{-4} at 12 T using the valence shown in Fig. 4, which gave the relative volume change $\Delta V/V \sim 1.94 \times 10^{-3}$. This was consistent with the $\Delta V/V \sim 1.8 \times 10^{-3}$ at around 12 T that was obtained from magnetostriction experiments. [23] This is the first clear evidence that the magnetovolume effect in $CeRu_2Si_2$ is due to the field-induced valence change.

The field variation of the valence observed in this study corresponds to the loss of itinerancy in terms of the Gützwiller approximation; magnetic fields reduce the value of $1 - n_f$. The relative reduction of the itinerancy was possibly evaluated as $\frac{\Delta n_f}{1-n_f(0\ T)} \sim \frac{0.005}{0.053} \sim 0.09$ around the metamagnetic transition (8-18 T); Δn_f corresponds to the change in the valence in a magnetic field and $n_f = 4 - v$. If a complete field-induced valence transition takes place, $\frac{\Delta n_f}{1-n_f(0\ T)}$ should be close to 1.0. It is actually about 0.7 in the Yb-based heavy fermion compound, $YbAgCu_4$.[25] The value of $\frac{\Delta n_f}{1-n_f(0\ T)} \sim 0.09$ in $CeRu_2Si_2$ suggests that the itinerancy is suppressed by only 9%. This is considerably smaller than the value expected for the complete valence transition. At 40 T, the value was $\frac{\Delta n_f}{1-n_f(0\ T)} \sim \frac{0.012}{0.053} \sim 0.23$, suggesting that the f electrons were still far from being completely localized. This evaluation is not changed if we consider the f^2 contribution that we did not take into account in our analysis. It is because the localization of the f-electron can be evaluated by the reduction of the f^0 component.

At a very high magnetic field, $1 - n_f = 0$ and the f electrons should become completely localized. If the magnetic field, H_L, where $1 - n_f = 0$ is simply estimated using an extrapolation of line (3) in Fig. 4 (a) to the position $v = 3.00$, then $H_L \sim 220$ T.

In conclusion, we have found that the Ce valence fluctuated at 1.8 K in $CeRu_2Si_2$ and that it decreased toward the pure trivalent state as the magnetic field was increased. The valence reduction, which corresponds to the metamagnetism at $H_m \sim 8$ T, was around 0.005, and was too small for the metamagnetism to be considered as the complete localization of the electrons. The valence changes gradually and thus cannot be a first order transition as has previously been suggested [16, 26]. The characteristic magnetic field dependence of n_f, or the Ce valence, can be understood by the gradual break down of the Kondo bound state. However, the relationship between the valence change and the metamagnetism is still not clear. $CeRu_2Si_2$ may be located close to the VTQCP, and it can be drawn closer by applying magnetic fields. Further theoretical studies are necessary to solve this problem.

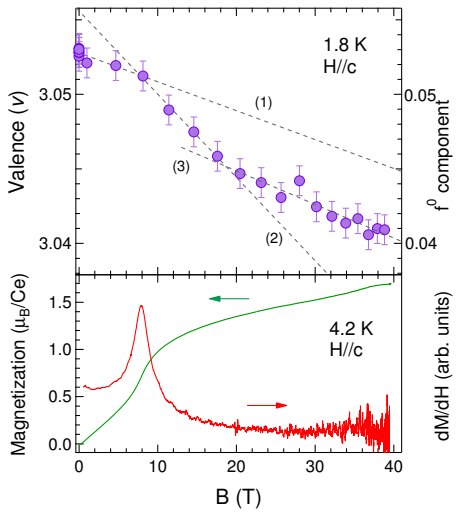

FIG. 4. (a) Magnetic field dependence of the Ce valence and the corresponding f^0 component at 1.8 K. The dashed lines (1), (2) and (3) show the slope of the valence change in low, medium and high magnetic field ranges, respectively. (b) Magnetic field dependence of the magnetization (M) and the field derivative (dM/dH) at 4.2 K.

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